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Indirect synthesis of a pair of formal methane activation products at a phosphane/borane frustrated Lewis pair†

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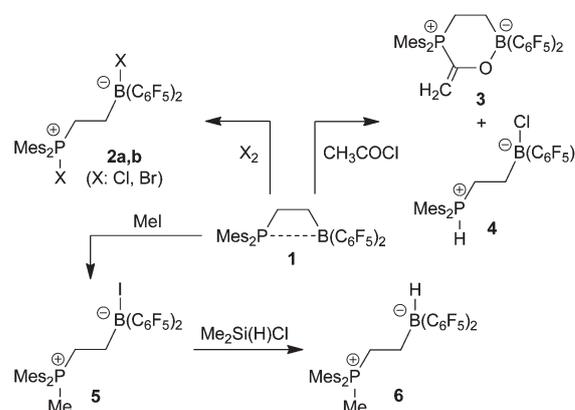
The regioisomeric formal $Mes_2PCH_2CH_2B(C_6F_5)_2$ FLP methane splitting products $Mes_2P(H)CH_2CH_2B(CH_3)(C_6F_5)_2$ and $Mes_2P(CH_3)CH_2CH_2B(H)(C_6F_5)_2$ were produced by indirect stepwise reactions. They were stable at 60 °C and were both characterized by X-ray diffraction. A DFT analysis revealed that their formation from the FLP and CH_4 would be endergonic by +6.9 and +3.6 kcal mol^{-1}, respectively, and it indicated that methane elimination from the zwitterionic products is kinetically hindered by barriers of 54.0 and 72.3 kcal mol^{-1}, respectively.

Frustrated Lewis pairs (FLPs) can effect a number of remarkable reactions.[1,2] Most noteworthy is the ability of many FLPs to split dihydrogen heterolytically in a metal-free situation and, consequently, to serve as efficient main-group element derived hydrogenation catalysts for a variety of organic (or even organometallic) substrates.[3] In addition, frustrated Lewis pairs add and sometimes activate a variety of small molecules, among them CO, CO_2, SO_2, NO, N_2O[4] and they have actively been involved in developing a few new and unprecedented reactions.[5,6] However, not too much is known about the reaction of FLPs with non-activated C–H bonds,[7,8] especially of the parent saturated hydrocarbon methane. We so far were not able to activate the CH_4 molecule by a reaction at a frustrated Lewis pair framework,[9] but we have now prepared the two possible methane C–H activation products at the ethylene-bridged intramolecular P/B FLP **1** by an indirect stepwise reaction pathway. From the isolated products we learned about the kinetic stability of the alleged CH_4/FLP activation products and, in combination with a DFT analysis, about the

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thermodynamic features of the pair of possible CH_4 + **1** reaction alternatives. These results will briefly be discussed in this account.

We had previously shown that the P/B FLP **1** reacted cleanly with the halogens Cl_2 or Br_2 to form the respective [P]Hal$^+$/[B]Hal$^-$ addition products **2a,b**.[10] With HCl compound **1** gave the respective [P]H$^+$/[B]Cl$^-$ product **4**[11] and with acyl chlorides the respective ketene addition products **3** [plus the [P]H$^+$/[B]Cl$^-$ co-product (**4**)] were formed.[12] We extended this series of FLP reactions now by the reaction of **1** with methyl iodide which cleanly gave the corresponding [P]CH$_3^+$/[B]I$^-$ product **5**, which we isolated in 87% yield as a colorless solid (see Scheme 1). We used compound **5** as the starting material for the synthesis of the respective [P]CH$_3^+$/[B]H$^-$ product **6**, one of the two formal CH_4/FLP splitting products.

Compound **5** shows the core heteroatom NMR resonances at δ −7.4 (^{11}B) and δ 26.7 (^{31}P), respectively. It features the typical NMR data of the pairs of mesityl groups at phosphorus and C_6F_5 groups at boron and the bridging ethylene unit (for details see the ESI†). The newly introduced methyl substituent at phosphorus gave rise to a ^{1}H NMR signal at δ 2.44 (d, $^2J_{PH}$ = 12.4 Hz; ^{13}C: δ 16.3, $^1J_{PC}$ = 53.2 Hz). The X-ray crystal structure
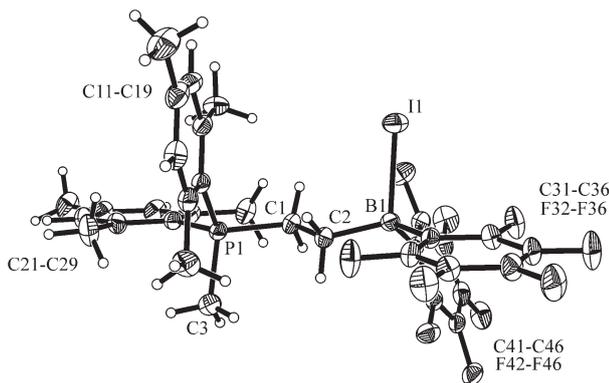

Scheme 1

Fig. 1 Molecular structure of compound **5** (thermal ellipsoids are shown at 30% probability). Selected bond lengths (Å) and angles (°): P1–C3 1.824(3), P1–C1 1.823(3), C1–C2 1.542(4), C2–B1 1.616(4), B1–I1 2.369(3), $\sum$B1^{CCC} 337.7, C1–P1–C3 103.3(2), C2–B1–I1 106.4(2), P1–C1–C2–B1 −169.4(2), θ C3–P1···B1–I1 −169.0.

analysis of compound **5** confirmed the attachment of the methyl group at phosphorus and the iodide substituent at boron. Both these heteroatoms show distorted tetrahedral coordination environments. The central P1–C1–C2–B1 unit shows an antiperiplanar conformational geometry (Fig. 1).

The iodide substituent at boron in compound **5** was exchanged for hydride by treatment with dimethyl-chlorosilane.[13] It was stirred with a *ca.* 2.4 times excess of the silane in dichloromethane solution for 30 min at r.t. Layering with pentane (−30 °C, 6 d) eventually gave the crystalline product **6**, which was isolated in 88% yield. The X-ray crystal structure analysis confirmed the successful removal of the halide and introduction of hydride at the pseudotetrahedral borate moiety ($\sum$B1^{CCC} 334.6°) of the zwitterionic compound (see Fig. 2). Again the central core of the molecule shows a slightly distorted antiperiplanar conformation (θ P1–C1–C2–B1 161.9(2)°), and the C3–P1–C1–C2 arrangement is gauche (θ 72.7(3)°).
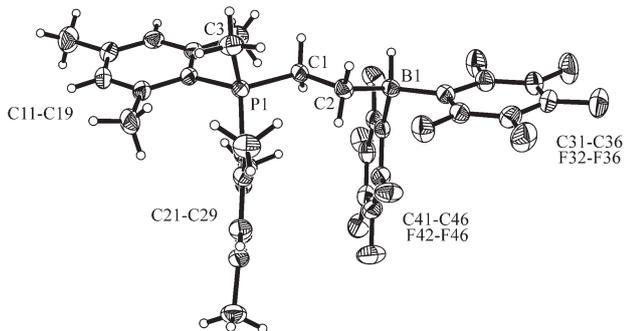

Fig. 2 A projection of the molecular structure of the zwitterionic [P]CH$_3^+$/[B]H$^-$ compound **6** (thermal ellipsoids are shown at 30% probability). Selected bond lengths (Å) and angles (°): P1–C3 1.800(3), P1–C1 1.807(3), C1–C2 1.541(4), C2–B1 1.640(4), C1–P1–C3 102.9(2), C1–C2–B1 107.1(2), P1–C1–C2 114.0(2), θ C3–P1···B1–H01 −77.6.

In d$_2$-dichloromethane the presence of the [B]–H group is confirmed in the ^{11}B NMR spectrum by the respective resonance at δ −19.7 (d, $^1J_{BH}$ ~ 90 Hz). The [P]–CH$_3$ group gives rise to NMR resonances at δ 25.8 (^{31}P), 2.39 (^{1}H, $^2J_{PH}$ = 12.5 Hz) and δ 16.0 (^{13}C, $^1J_{PC}$ = 54.3 Hz) and we have monitored the typical NMR features of the –CH$_2$–CH$_2$– bridge and the pairs of mesityl groups at phosphorus and C$_6$F$_5$ substituents at boron (for details see the ESI†).

We also explored the stepwise formation of the other possible formal FLP methane C–H splitting product, namely the ethylene-bridged zwitterionic [P]H$^+$/[B]CH$_3^-$ compound **9**. This was prepared by using an organometallic route that we had recently developed.[14] We had shown that treatment of Cp$_2$Zr(CH$_3$)$_2$ with the FLP **1** resulted in a clean methyl anion abstraction from the zirconium atom by the active boron Lewis acid to form complex **8**. The X-ray crystal structure analysis had confirmed the contact ionic pair structure of compound **8** (see Scheme 2).[15] We have now generated the salt **8** *in situ* and hydrolyzed it directly without further characterization. Workup eventually gave the new [P]H$^+$/[B]CH$_3^-$ product **9** as a white solid, which we isolated in 95% yield.

Compound **9** shows a ^{31}P NMR [P]–H resonance at δ −2.1 with a typical large coupling constant of $^1J_{PH}$ ~ 470 Hz (the corresponding ^{1}H NMR [P]–H signal is at δ 7.36). The [B]–CH$_3$ moiety gives rise to a broadened ^{1}H NMR feature at δ 0.13 (^{13}C: δ 9.4; ^{11}B: δ −12.7). As expected, we monitored three ^{19}F NMR signals of the *o*-, *p*-, and *m*-F atoms of the pair of C$_6$F$_5$ groups at boron with a typical small $\Delta\delta^{19}$F$_{m,p}$ = 2.2 ppm chemical shift difference, and we observed the typical ^{1}H/^{13}C NMR signals of the pair of mesityl substituents at phosphorus and the bridging –CH$_2$–CH$_2$– group [^{1}H: δ 2.61 (PCH$_2$), δ 1.21 (CH$_2$B); ^{13}C: δ 25.0 ($^1J_{PC}$ = 34.1 Hz), δ 23.0 (br m)].

The X-ray crystal structure analysis showed the presence of a tetracoordinated boron atom that had the methyl substituent attached to it. The phosphorus atom is protonated ($\sum$P1^{CCC} 343.9°) and the central P1–C1–C2–B1 unit shows a close to antiperiplanar conformational arrangement (θ −178.3(3)°), whereas the C3–B1–C2–C1 unit is close to gauche oriented (θ 64.7(5)°) (see Fig. 3).

We briefly investigated the thermal stability of the compounds **6** and **9**. Both turned out to be stable at 60 °C in dichloromethane solution for prolonged periods of time (24 h), compound **6** was even stable at 90 °C, whereas compound **9**
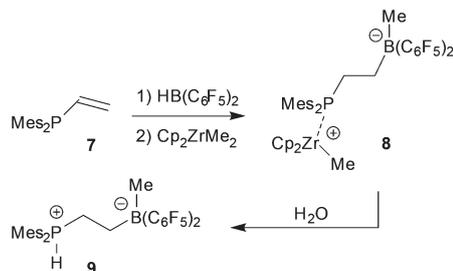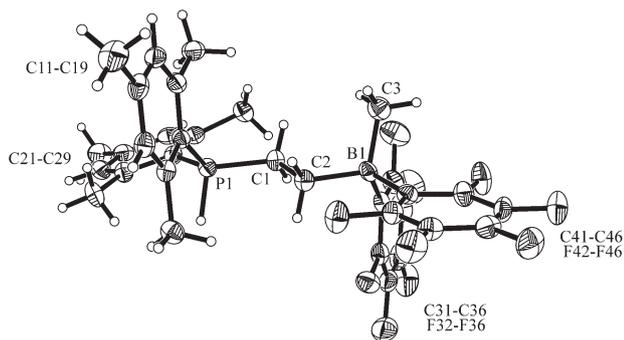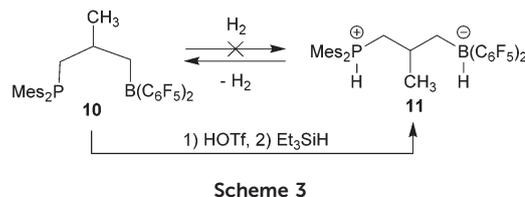

Scheme 2

Fig. 3 A view of the molecular structure of the $[P]H^+/[B]CH_3^-$ compound **9** (thermal ellipsoids are shown at 30% probability). Selected bond lengths (Å) and angles (°): P1–C1 1.796(5), C1–C2 1.528(6), C2–B1 1.658(7), B1–C3 1.646(7), P1–C1–C2 111.7(3), C2–B1–C3 108.0(4), C1–C2–B1 110.6(4), θ H01–P1···B1–C3 –175.6.

decomposed unspecifically at this temperature (for details and the depicted spectra of these experiments see the ESI†).

Since our study had shown that both of the formal methane CH activation products **6** and **9** were stable at 60 °C in dichloromethane solution, we checked whether CH_4 would react with the P/B FLP **1** under these conditions to give either of these two compounds. However, slowly heating of **1** in the presence of methane (10 bar) to 60 °C and keeping the mixture at this temperature for 20 h did not give any indication of the formation of these products. We only found the usual unspecific decomposition of **1** under these conditions (see the ESI† for details).

The FLP **1**/CH_4 systems were characterized by DFT analysis. The thermodynamics of the reaction of **1** with CH_4 were calculated with our established protocol[16,17] employing PW6B95-D3(BJ)/def2-QZVP electronic energies. Ro-vibrational free energies from HF-3c harmonic frequencies and solvation free energy corrections for dichloromethane from COSMO-RS(2012 parametrization) were computed at $T = 298.15$ K.

It turned out that the Gibbs free energies of both reactions were positive, namely ΔG (298 K) = +6.9 kcal mol^{-1} for the hypothetical **1** + CH_4 to **9** and ΔG (298 K) = +3.6 kcal mol^{-1} for the **1** + CH_4 to **6** conversion, i.e. both the methane C–H splitting reactions starting from the ethylene-bridged P/B FLP **1** are endergonic. Given that the thermodynamically favorable methane liberation is not observed in the experiment, effective kinetic hindrance of the cleavage of CH_4 from both **6** and **9** must be assumed. In fact, calculations at the above mentioned level of theory reveal that the barrier $\Delta G^{\ddagger}$ (298.15 K) for the methane liberation is very high in both cases, being +72.2 kcal mol^{-1} for **6** and +54.0 kcal mol^{-1} for **9**, respectively (see the ESI† for details). In both transition states, it is the formally cationic substituent attached to phosphorus which is dissociated and has approached the formally anionic substituent attached to boron. Furthermore, the methane liberation proceeds through inversion of the methyl group, yielding an almost free, planar methyl group (formally a carbocation) in the transition state geometry for the methane liberation from **6**, while

Scheme 3

for **9**, the somewhat planarized methyl group (formally a carbanion) is still close to the boron atom. The presence of the planarized methyl group likely results in the very high barriers. It seems that it is this kinetic protection that essentially makes the pair **6** and **9** experimentally observable and even isolable under our typical reaction conditions. This is in stark contrast to e.g. the rapid H_2 formation from the endergonic FLP H_2-splitting product **11** that was in a conceptually related way prepared by an indirect stepwise alternative pathway from the inactive trimethylene-bridged P/B FLP **10** (see Scheme 3).[18]

We might speculate that FLP derived analogues of either **6** or **9** might eventually become available by a methane CH activation process at much high temperature, taking into account the relatively small endergonic energy amount of these systems. This would, however, require the availability of suited thermally very robust FLPs, systems much more stable than **1** and its congeners. We have just recently reported the beginning of a development towards such robust FLP systems.[19]

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